The Nanopore Inner-Sphere Enhancement (NISE) Effect and its Role in Sodium Retention

Dr. Daniel R. Ferreira

Meiji University, Tokyo, Japan

May 12, 2016

Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

II. **Investigation** of the NISE Effect for cation adsorption on zeolites

III. **Confirmation** of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

IV. **Application** of the NISE Effect in a Column Study

Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

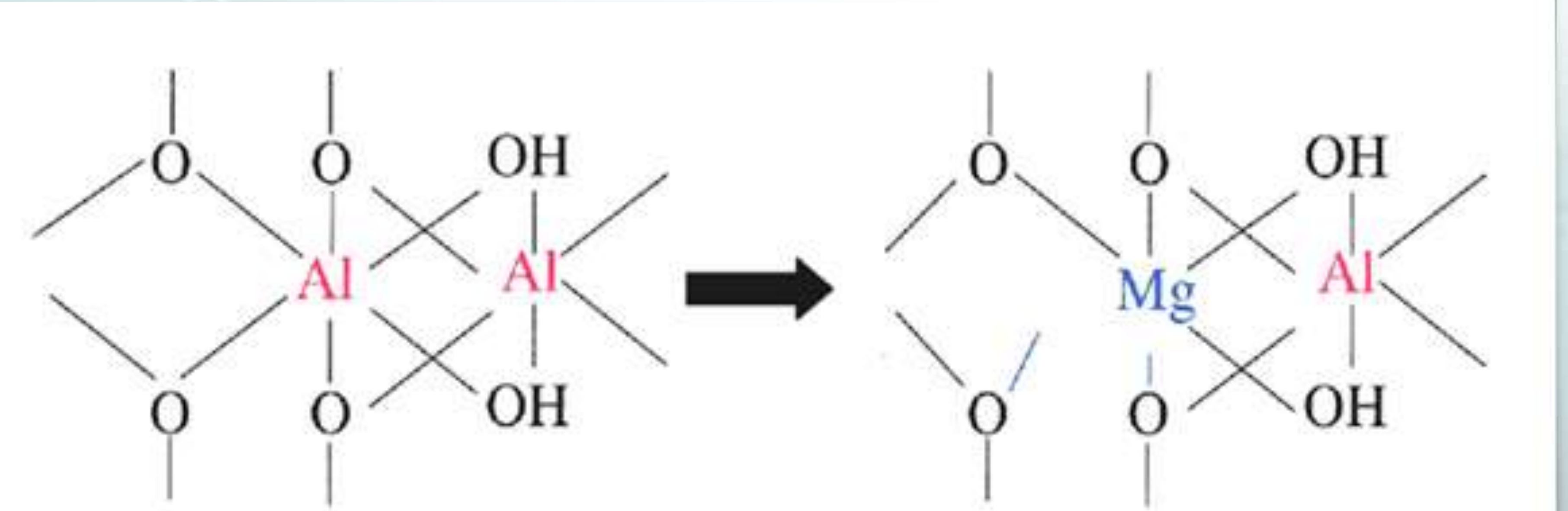
II. Investigation of the NISE Effect for cation adsorption on zeolites

III. Confirmation of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

IV. Application of the NISE Effect in a Column Study

Ion Adsorption

Isomorphous substitution creates mineral charge imbalance

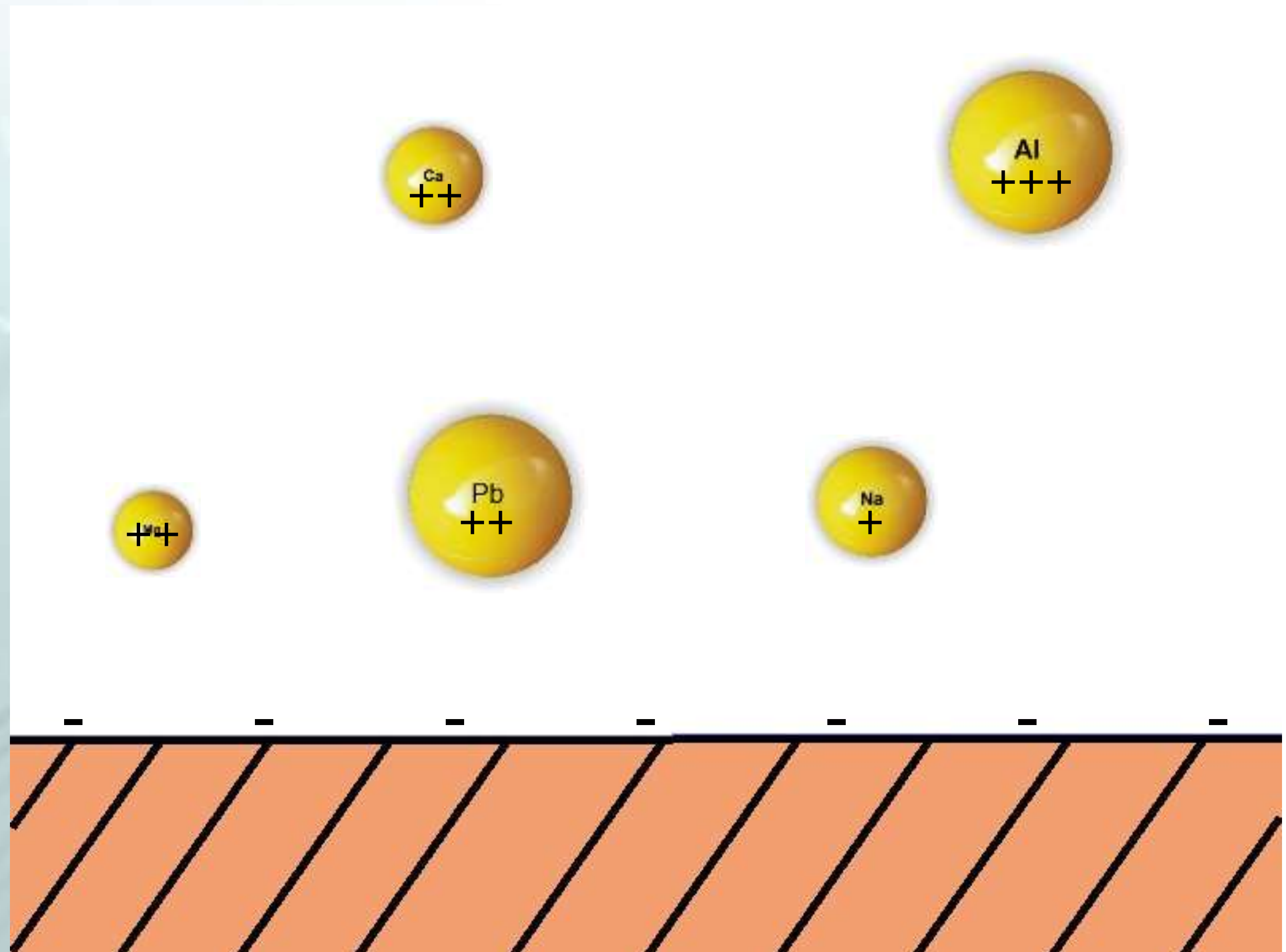


http://www.tankonyvtar.hu/en/tartalom/tamop425/0032_talajtan/images/new/17.bmp

Negative charge imbalances balanced by adsorbing cations

Ion Adsorption

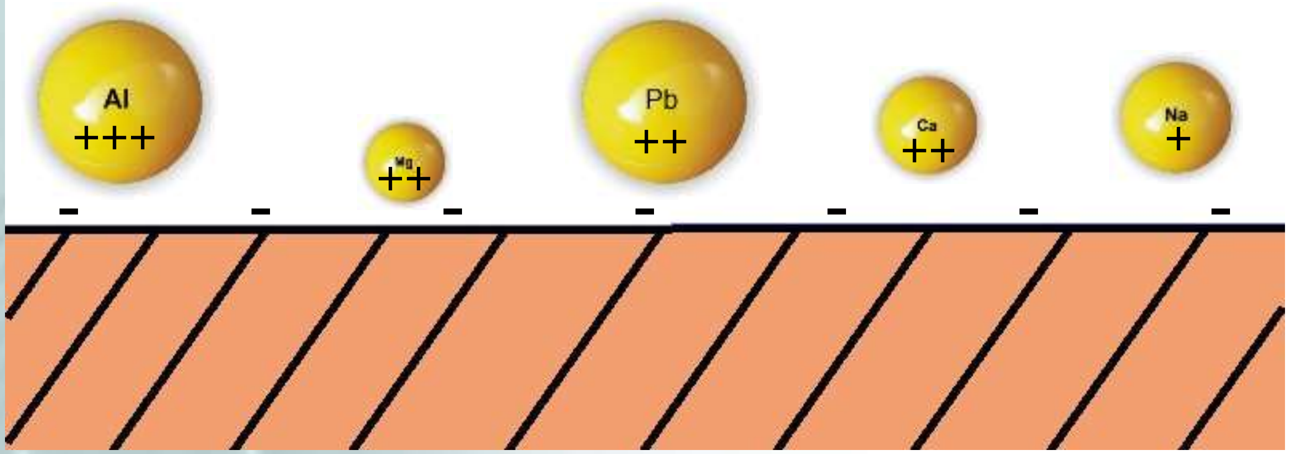
Groundwater



Negatively charged mineral surface

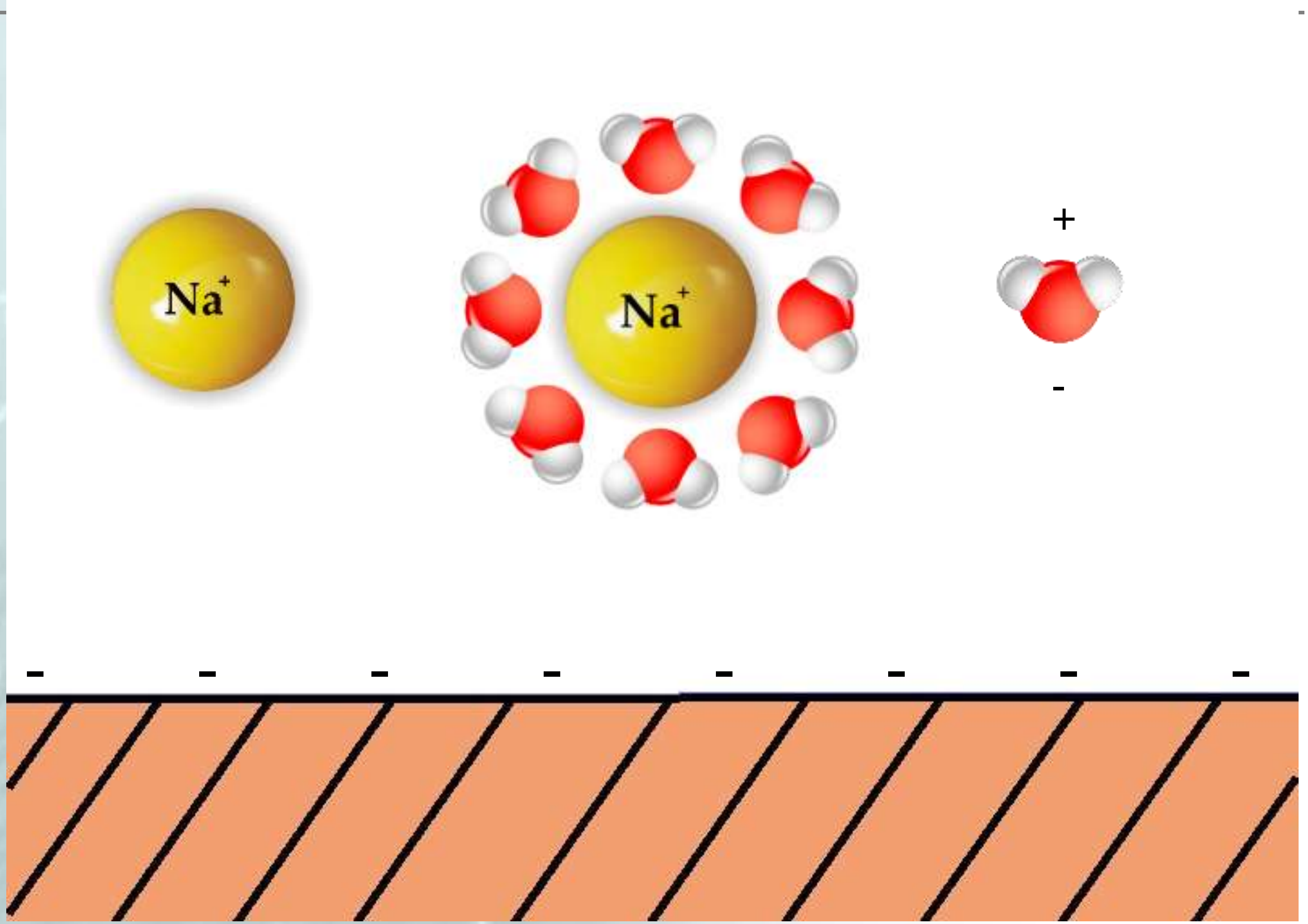
Ion Adsorption

Groundwater



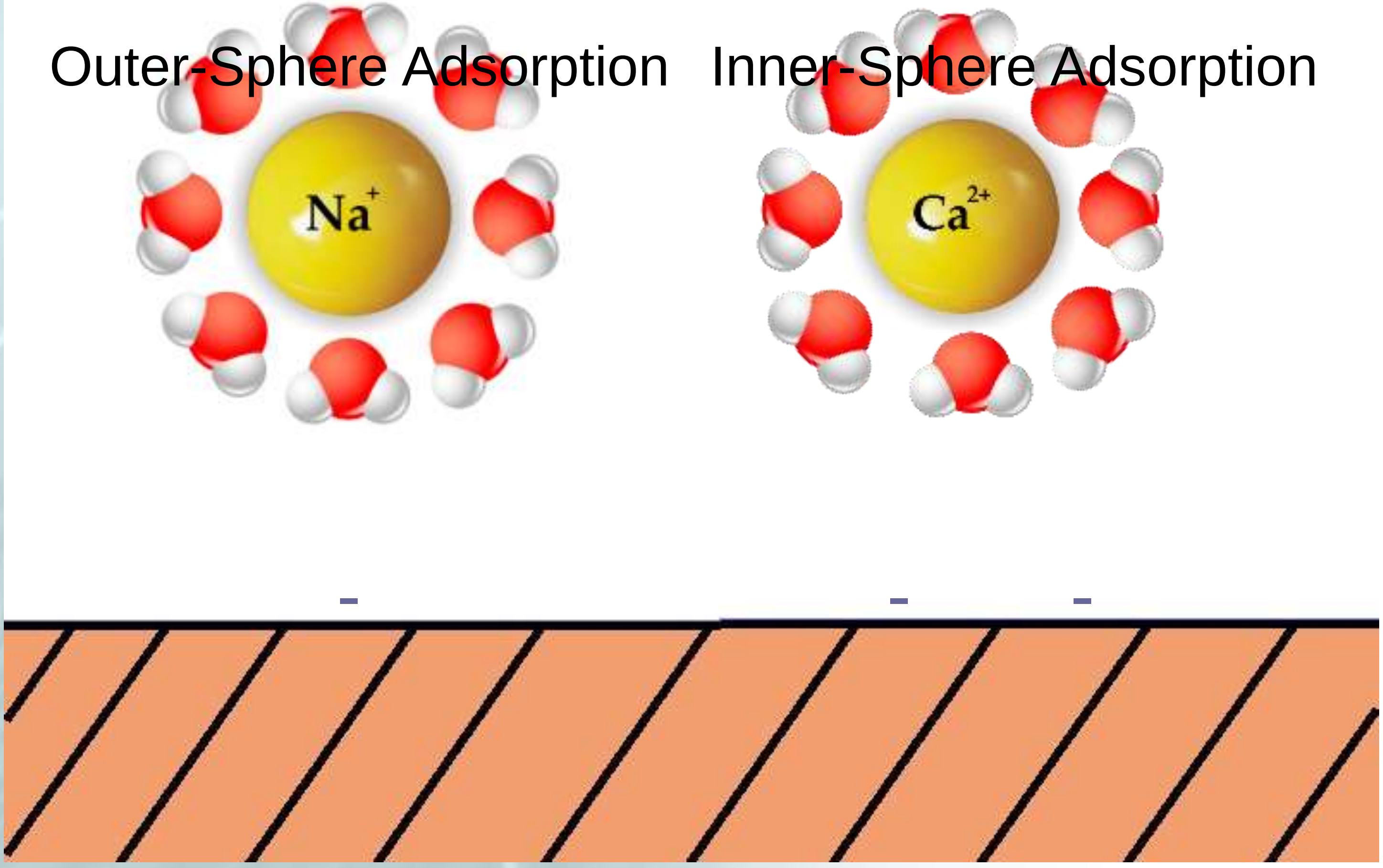
Negatively charged mineral surface

Ion Adsorption



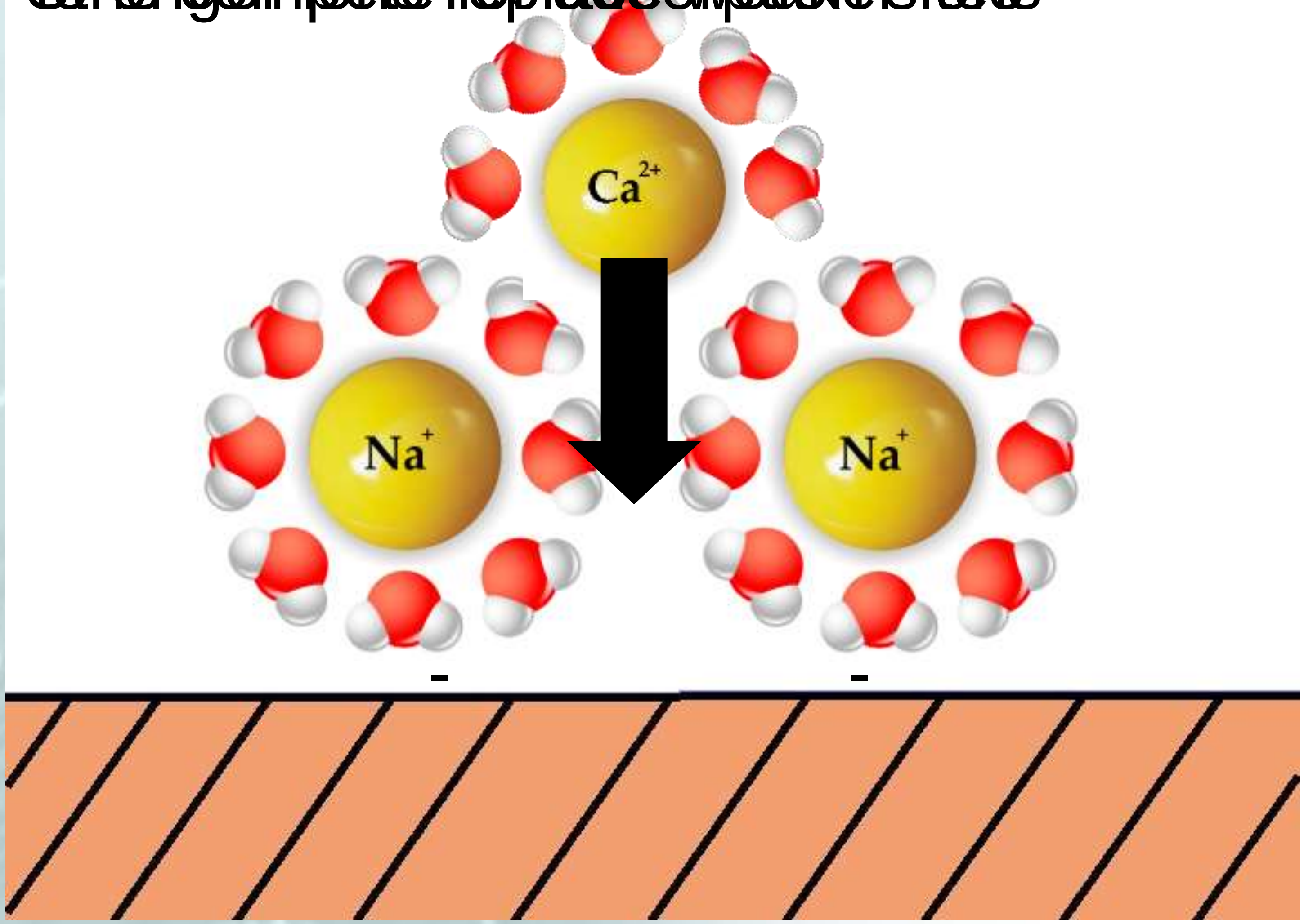
Ion Adsorption

The Na and Ca both want to adsorb, but they use different mechanisms



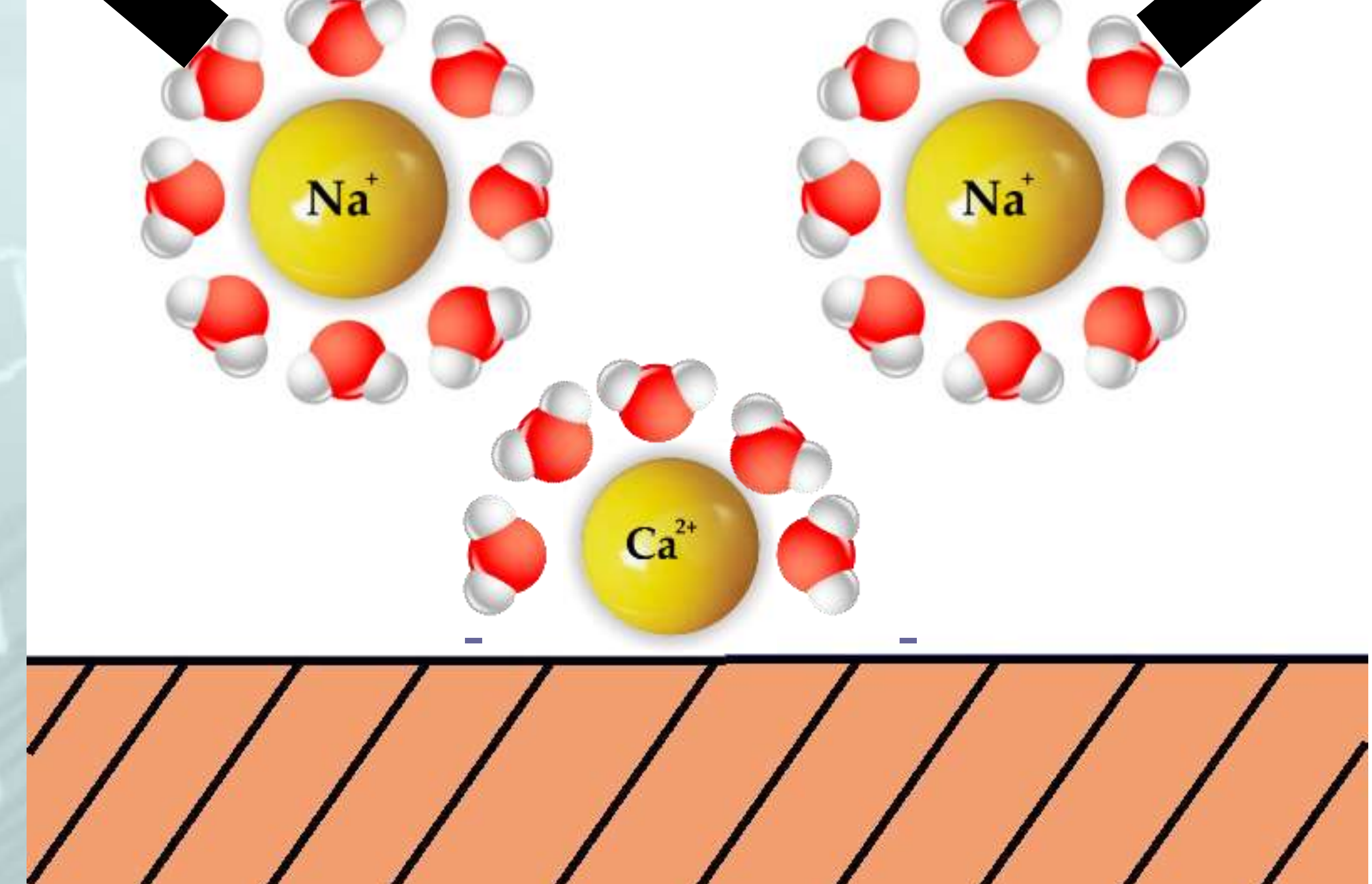
Ion Exchange

- Ions compete for adsorption sites
- Stronger ions replace weaker ions



Ion Exchange

- Weaker ions move from surface to solution

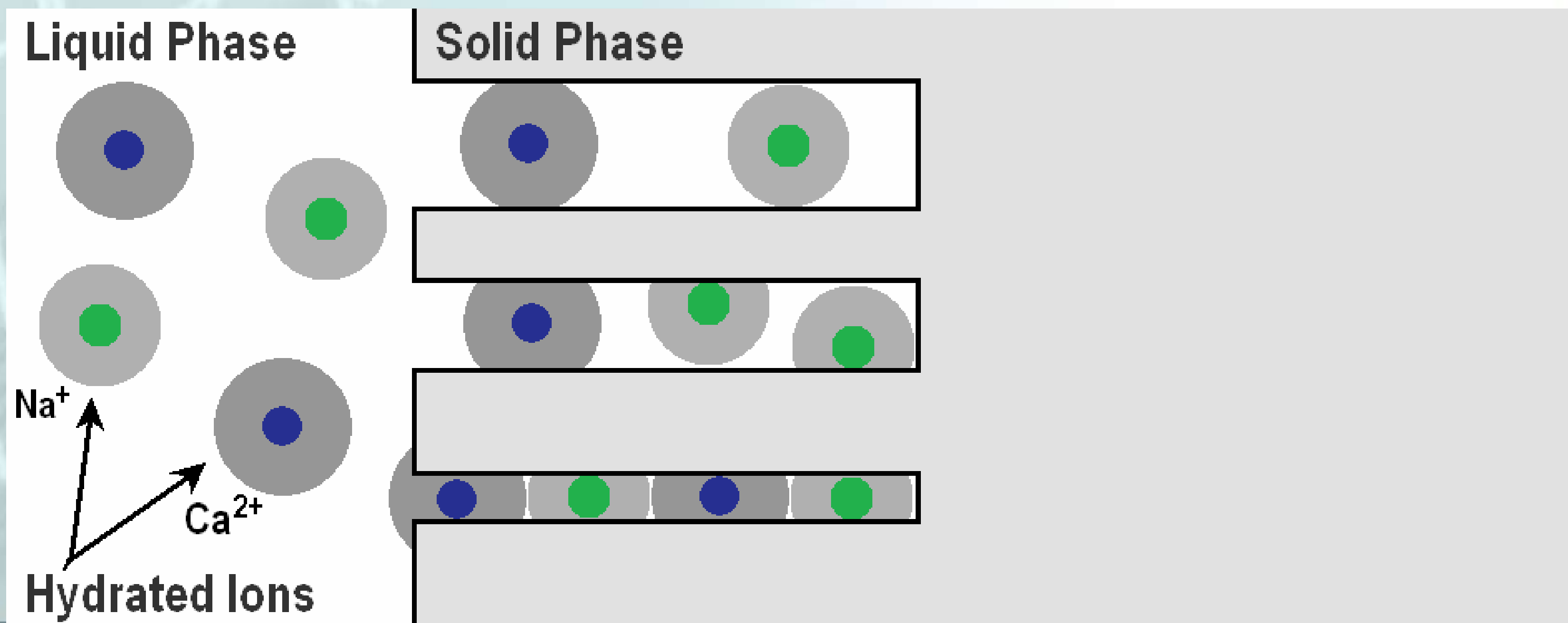


Nanopores

- Nanopores change the rules of ion adsorption / ion exchange
  - Ionic radius and hydration strength become very important

The NISE Effect
Nanopores

- Nanopores change the rules of ion adsorption / ion exchange
    - Ionic radius and hydration strength become very important



Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

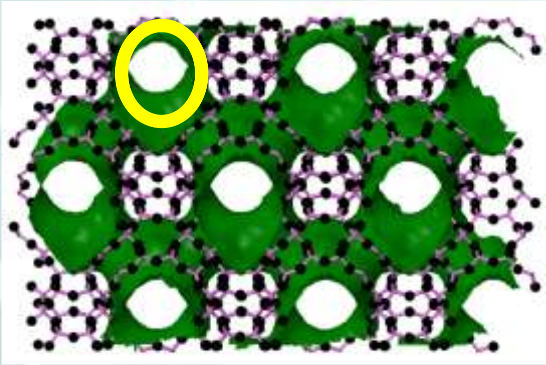
II. **Investigation** of the NISE Effect for cation adsorption on zeolites

III. Confirmation of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

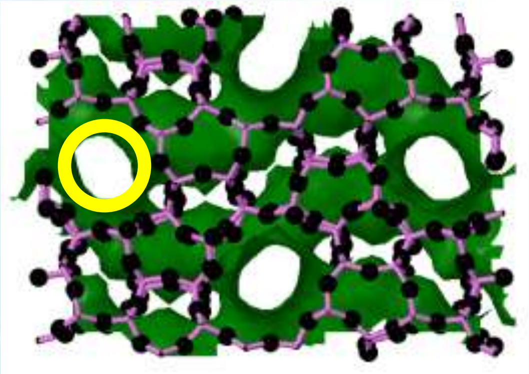
IV. Application of the NISE Effect in a Column Study

Cation Adsorption on Zeolites

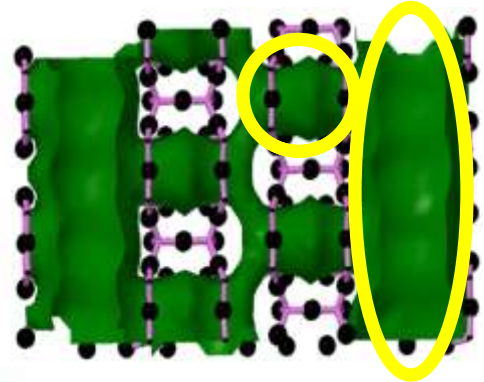
- Zeolites are nanoporous aluminosilicate minerals



Zeolite Y:
Large pores
0.74x0.74 nm



ZSM-5: Medium pores
0.51x0.55 nm
0.53x0.56 nm



Mordenite: Large & Small pores
0.70x0.65 nm
0.26x0.57 nm

- The dimensions of the pores are predictable and fixed. This makes zeolites ideal for studying pore size effects.

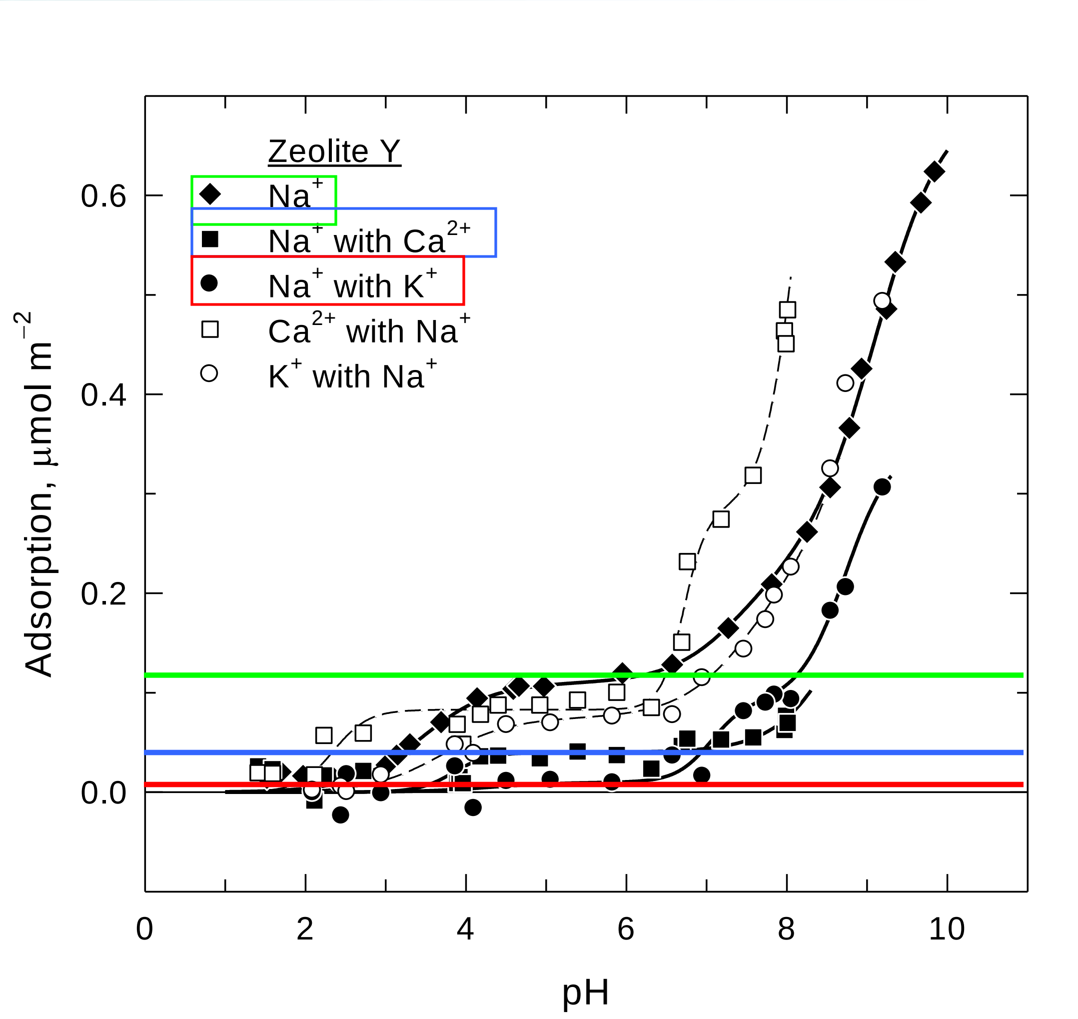
Cation Adsorption on Zeolites

- Adsorption studies were conducted on three zeolites to confirm the NISE model predictions
  - Zeolites mixed in aqueous solution with H_2O, NaOH, and HCl. $CaCl_2$ and KCl added to some mixtures as competitors.
  - Mixtures were agitated 18-20 hours, then centrifuged.
  - Liquid separated, analyzed for pH and [Na], [Ca], and [K]

	Na	K	Ca
Charge	+1	+1	+2
Ionic D (nm)	0.248	0.318	0.240
ΔG^* (kJ mol^{-1})	-368	-296.5	-1529

Hydration energy values from Hummer et al., 1996. Ionic diameter values from Schulthess, 2005.

Zeolite Y (large pores)



Pore sizes:

Pore 1 – 0.74x0.74 nm

Surface area:

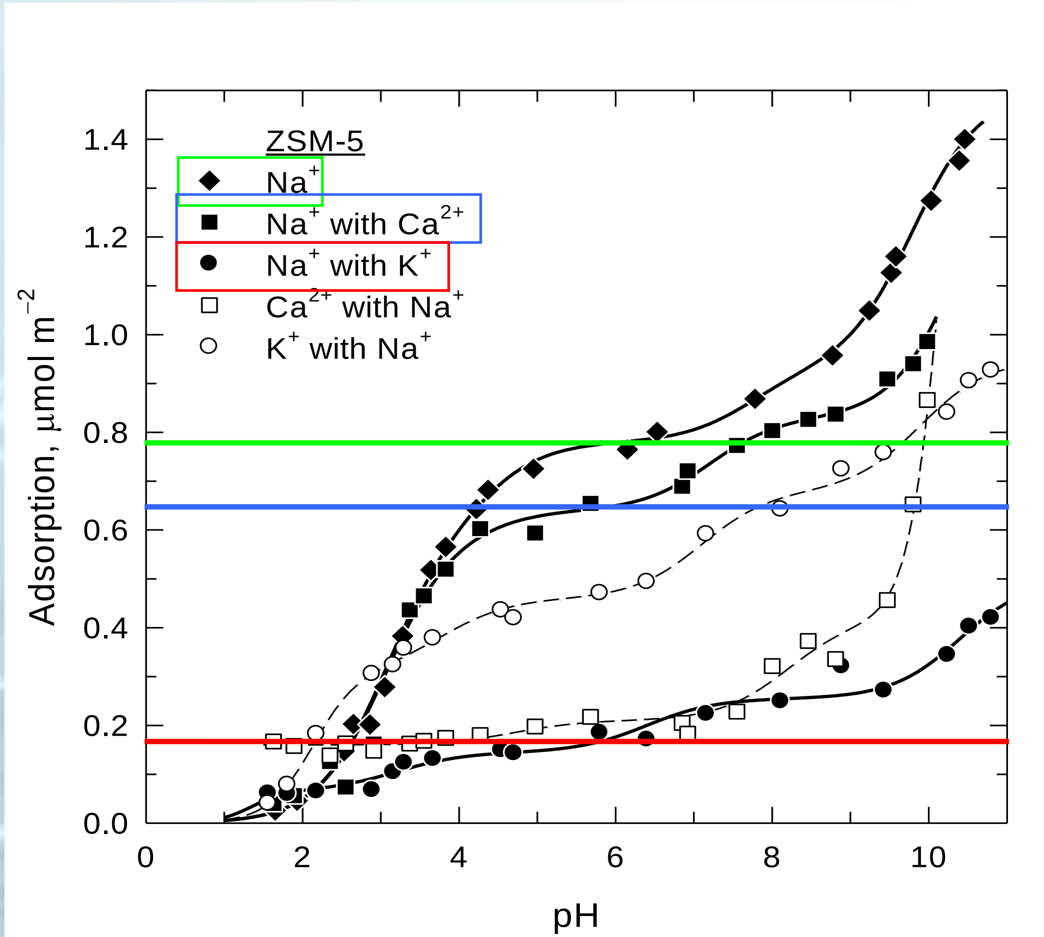
700 m^2 / g

CEC:

0.09 $umol_c$ / m^2

Affinity Sequence: Na ~ Ca ~ K

ZSM-5 (Medium pores)



Pore sizes:

Pore 1 – 0.51x0.55 nm

Pore 2 – 0.53x0.56 nm

Surface area:

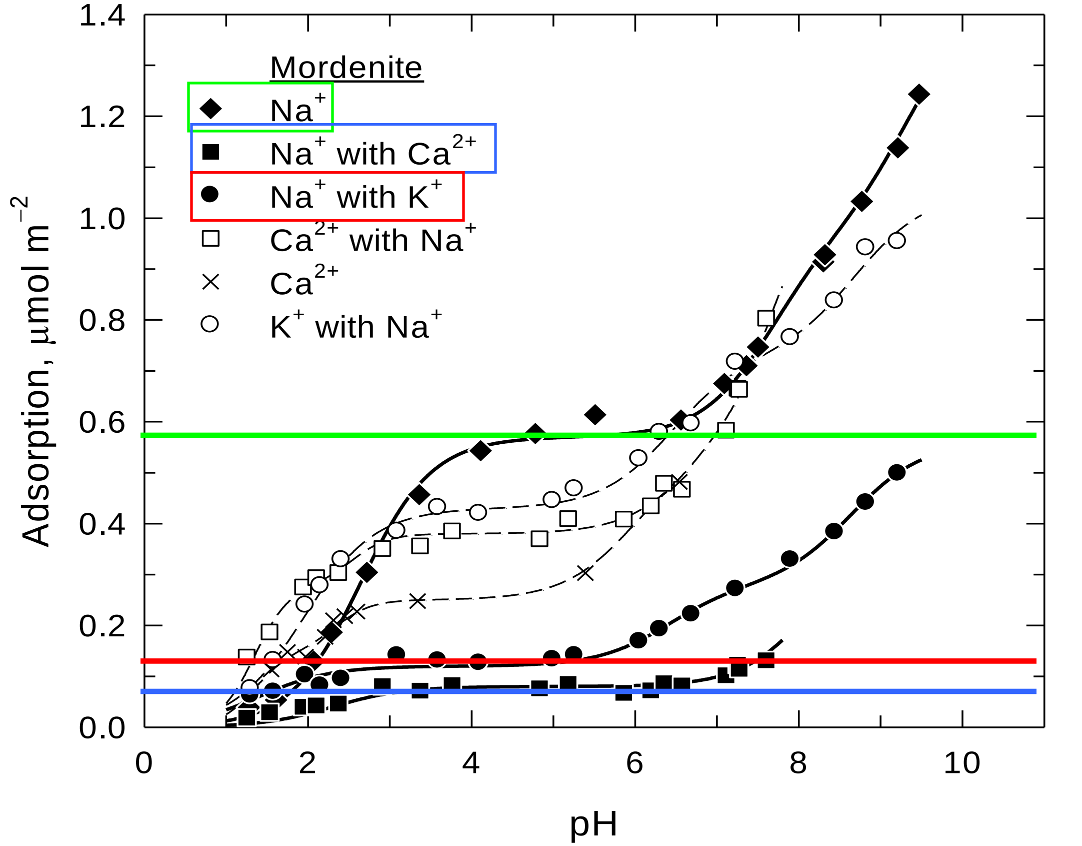
425 m^2 / g

CEC:

0.589 $umol_c$ / m^2

Affinity Sequence: K > Na >> Ca

Mordenite (large & small pores)



Pore sizes:

Pore 1 – 0.70x0.65 nm

Pore 2 – 0.26x0.57 nm

Surface area:

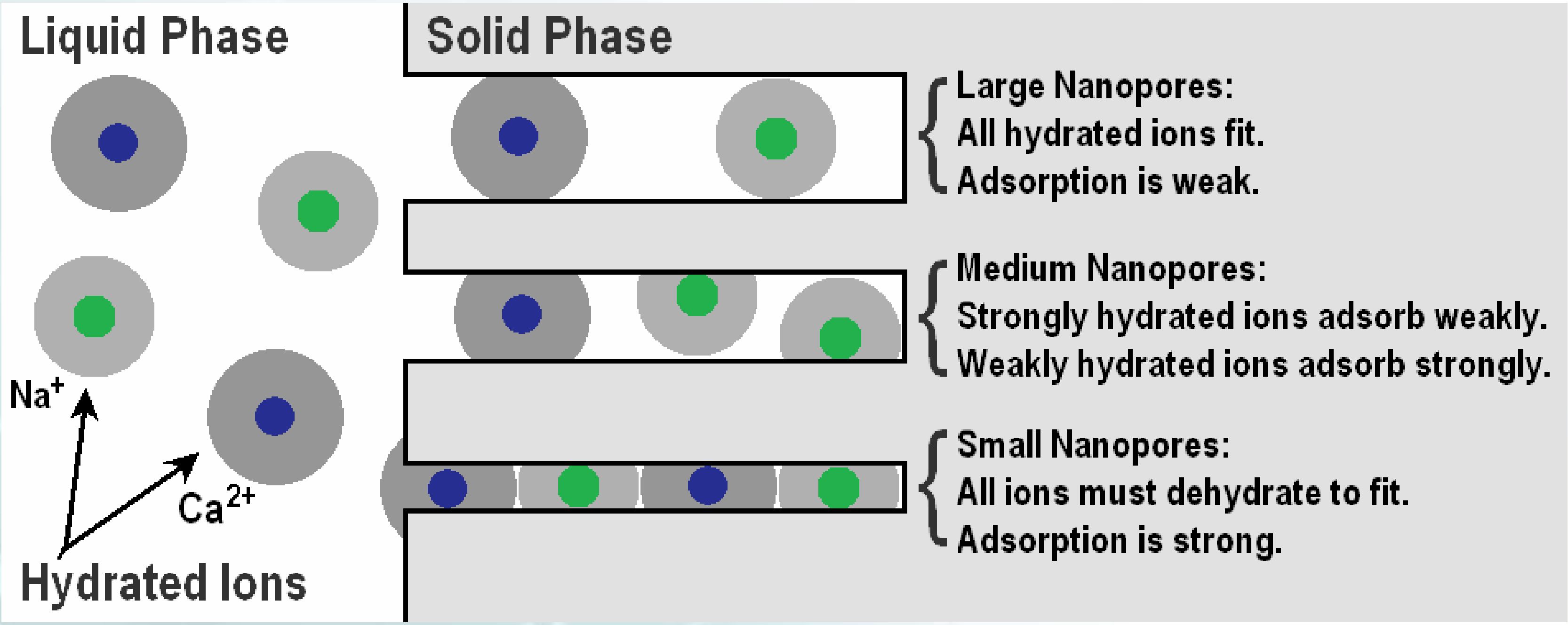
500 m^2 / g

CEC:

0.491 $umol_c$ / m^2

Affinity Sequence: Ca ~ K > Na

The NISE Effect



Adsorption studies of Na^+, K^+, and Ca^{2+} showed:

- Large pores – All 3 cations weak
- Medium pores – Monovalent cations strong, divalent cation weak
- Small pores – All 3 cations strong

Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

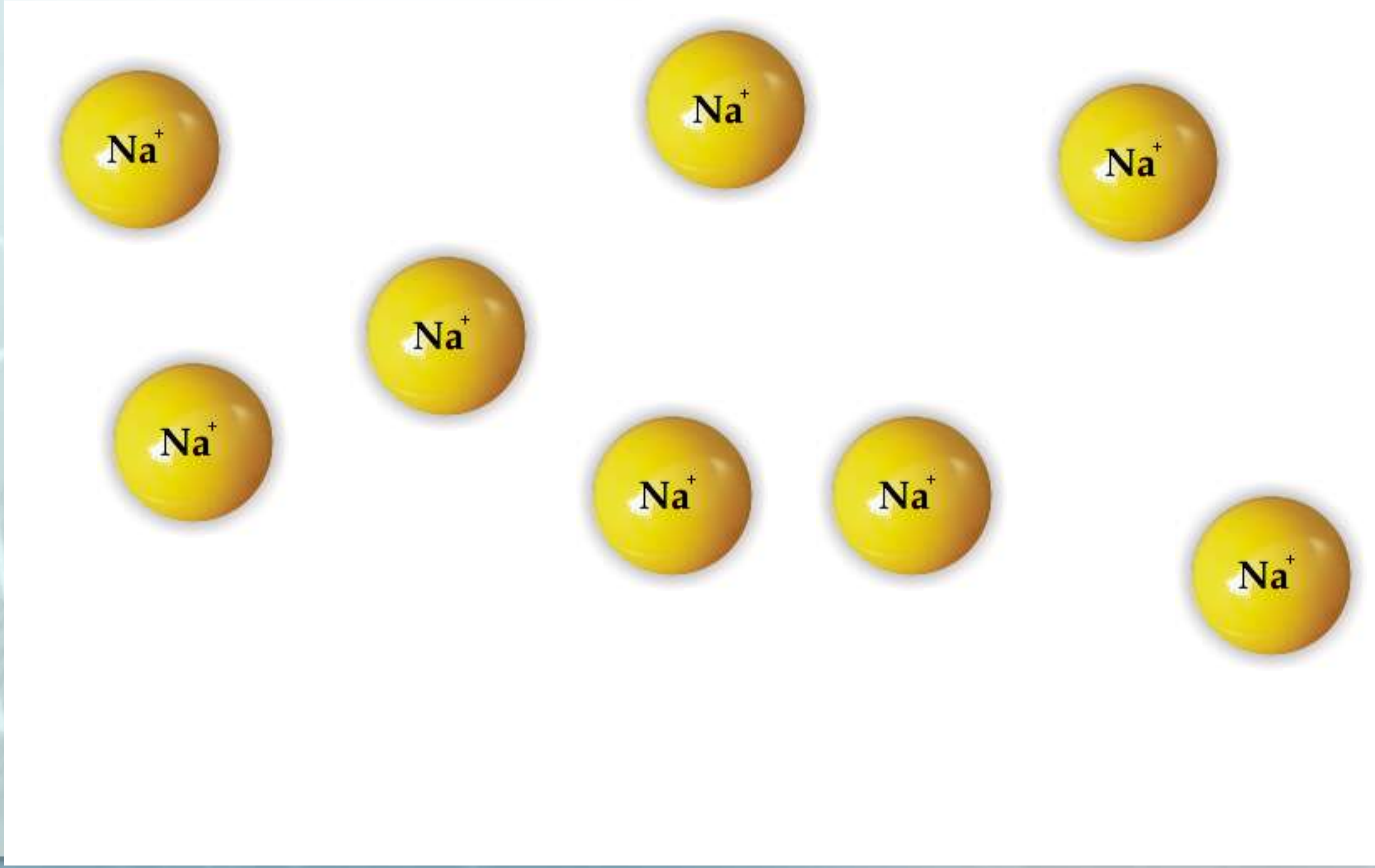
II. Investigation of the NISE Effect for cation adsorption on zeolites

III. **Confirmation** of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

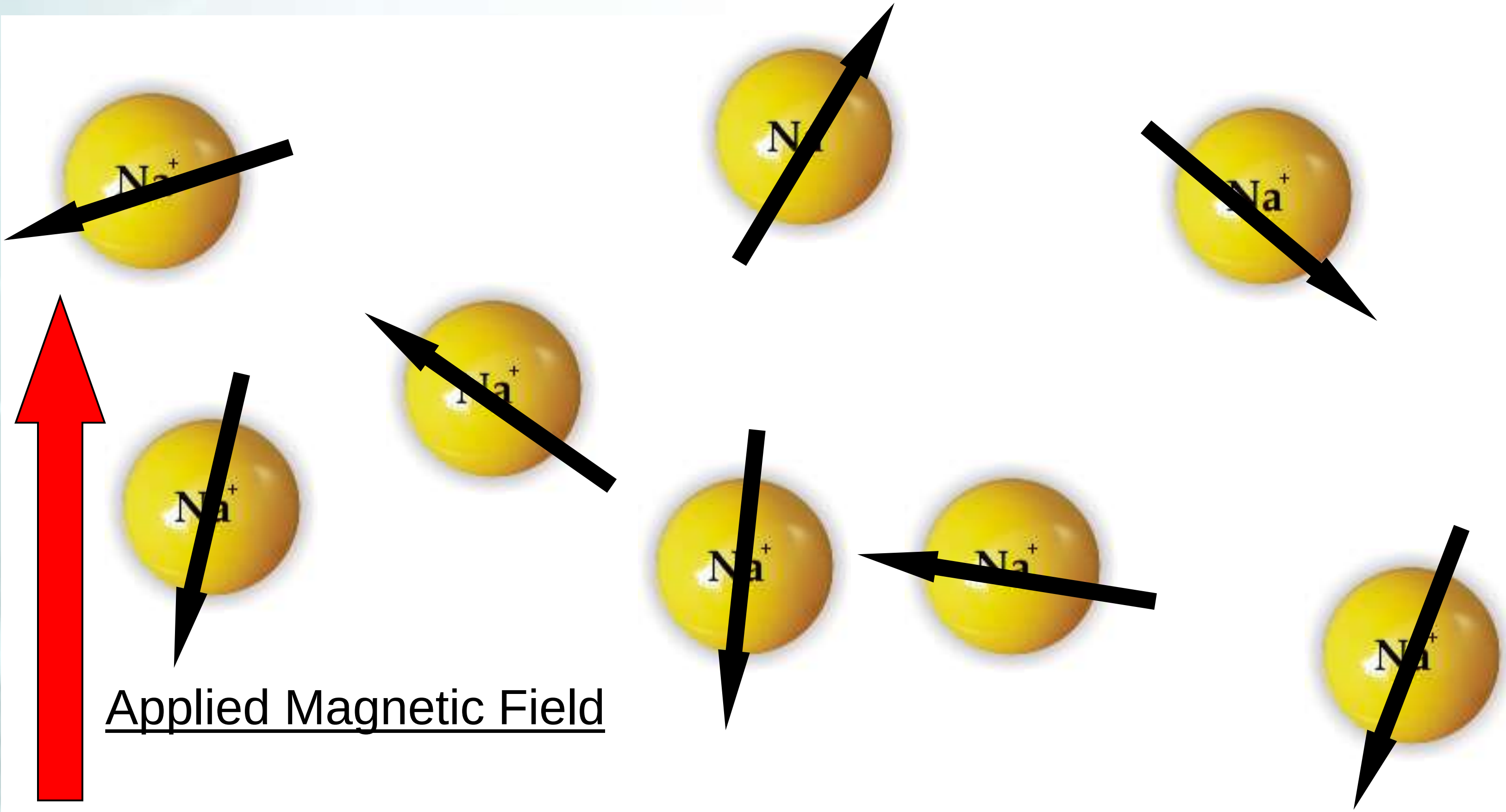
IV. Application of the NISE Effect in a Column Study

Nuclear Magnetic Resonance (NMR)

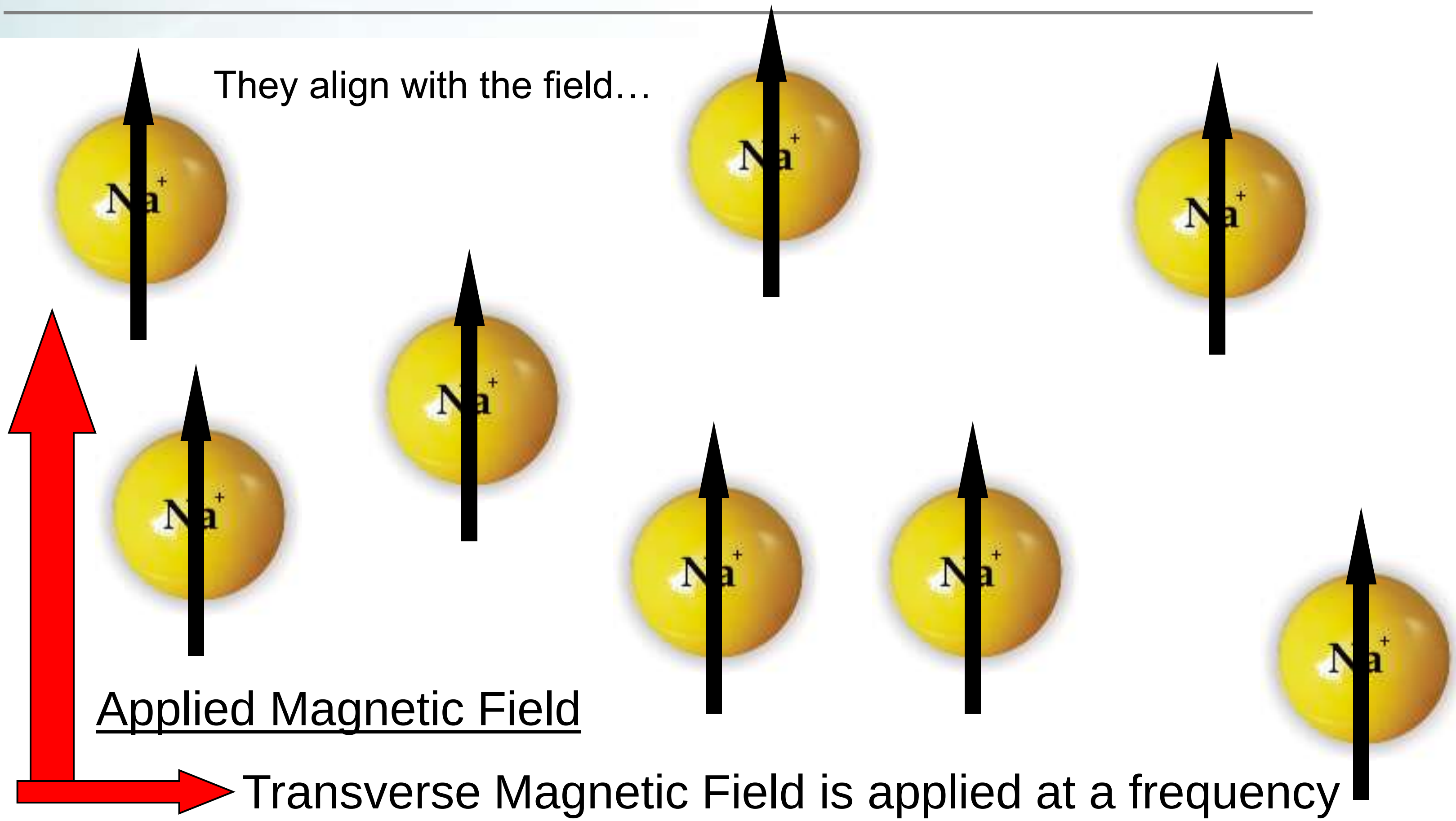
Sodium under NMR



Sodium under NMR

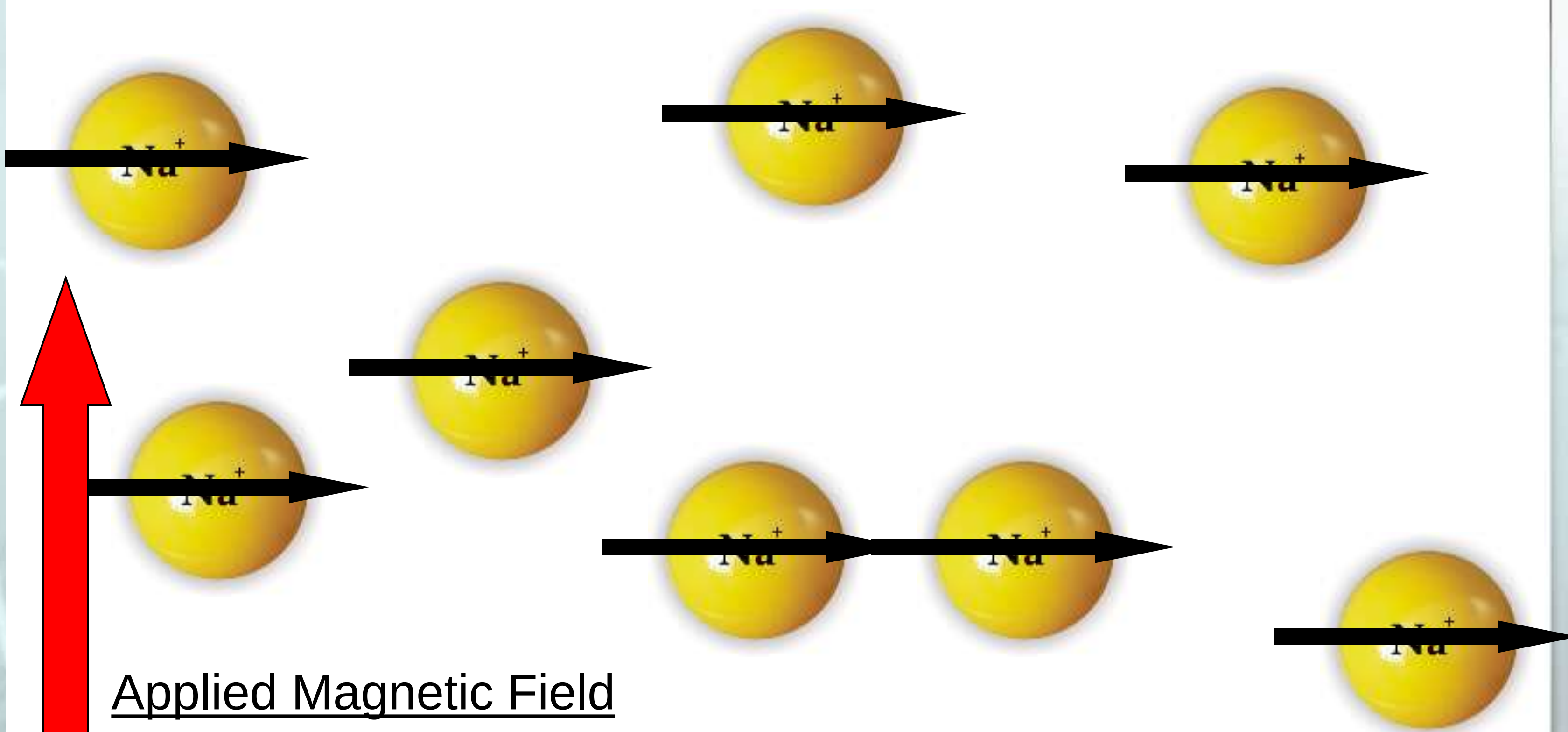


Sodium under NMR



Transverse Magnetic Field is applied at a frequency in resonance with precession, creating a torque.

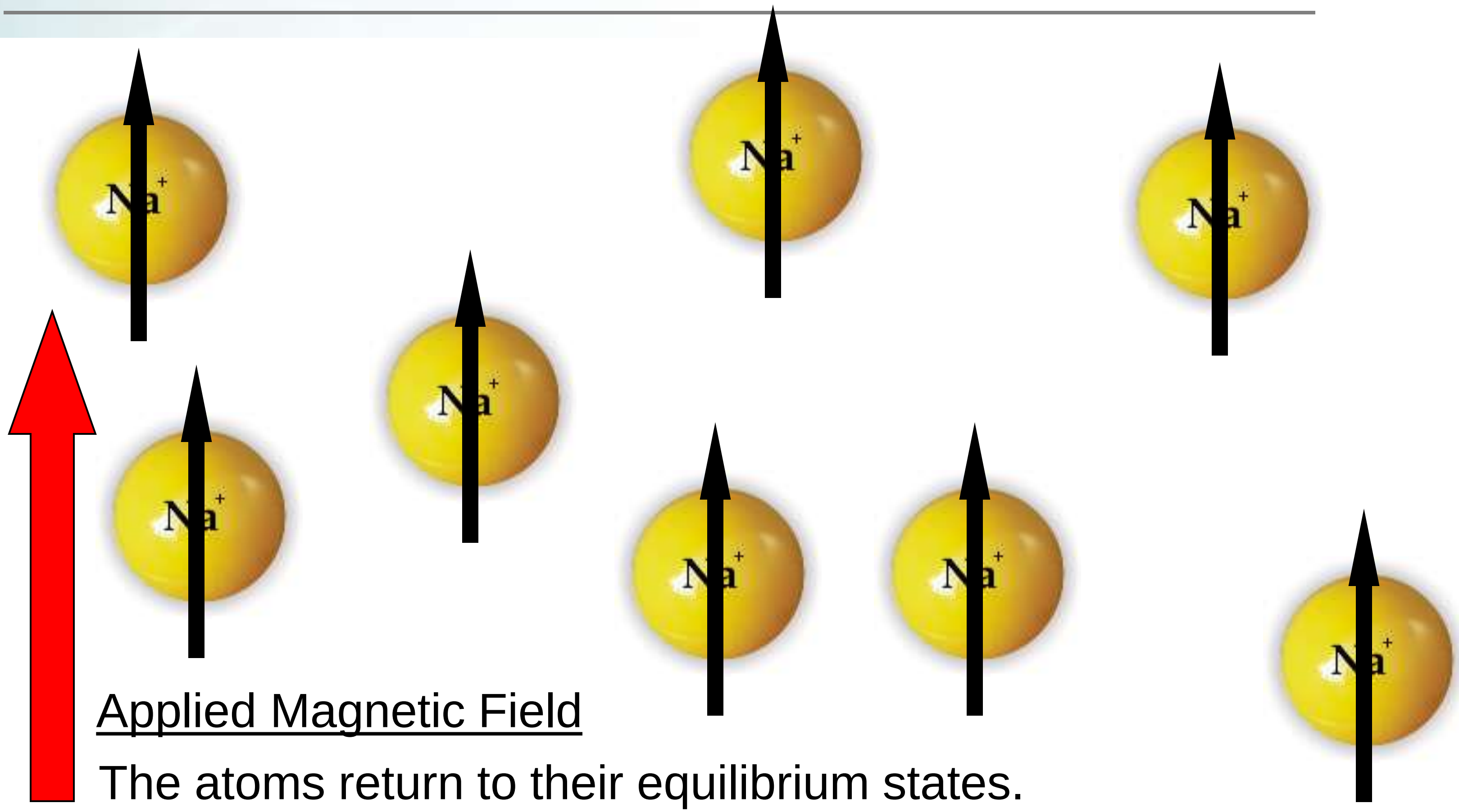
Sodium under NMR



Transverse Magnetic Field is applied at a frequency in resonance with precession, creating a torque.

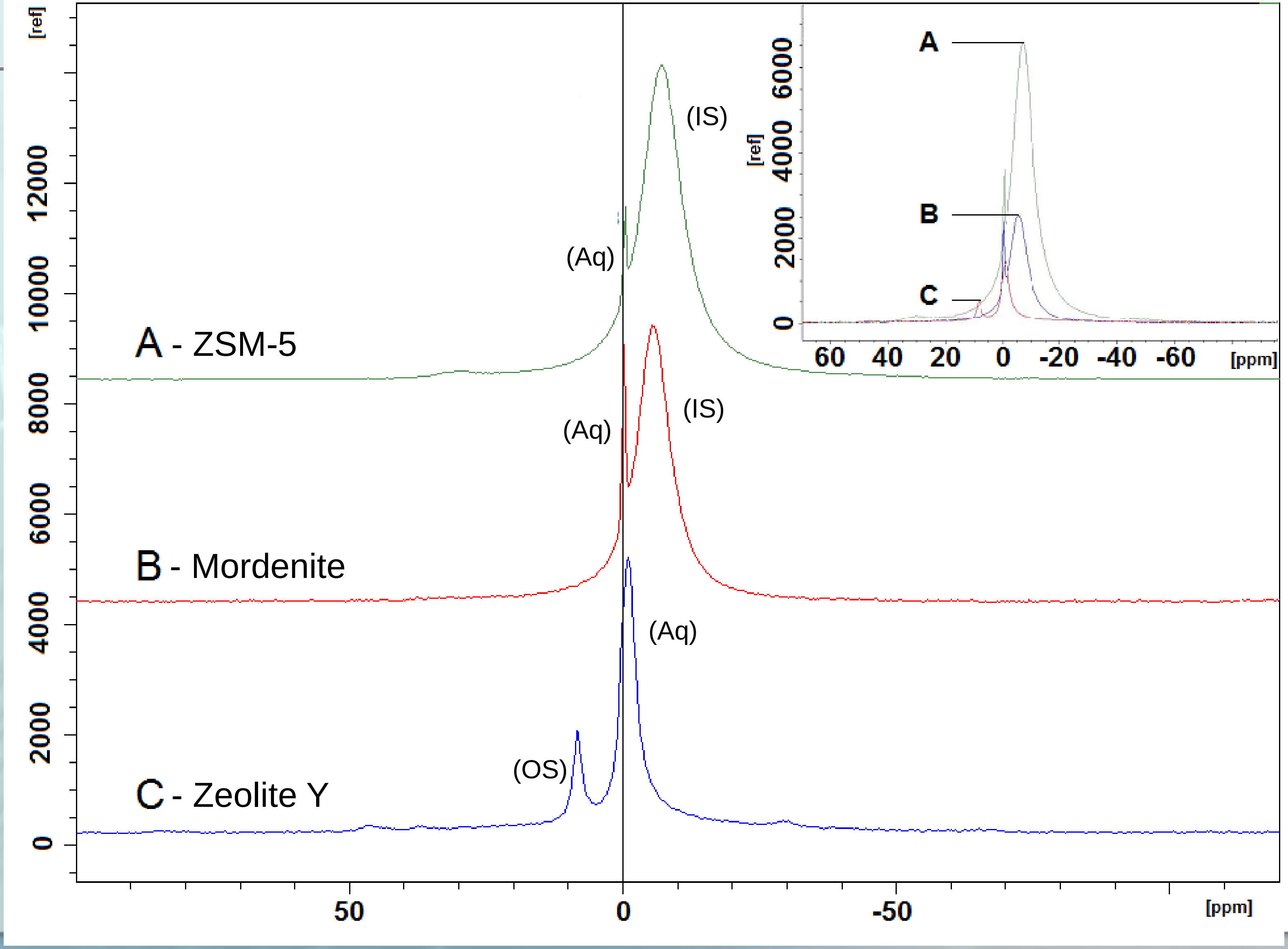
When the Transverse Magnetic Field is released…

Sodium under NMR



The atoms return to their equilibrium states.

NMR Spectra



[ref]
0
2000
4000
6000
8000
10000
12000
A - ZSM-5
B - Mordenite
C - Zeolite Y
(IS)
(Aq)
(IS)
(Aq)
(Aq)
(OS)
50
0
-50
[ppm]
A
B
C
[ref]
0
2000
4000
6000
60
40
20
0
-20
-40
-60
[ppm]

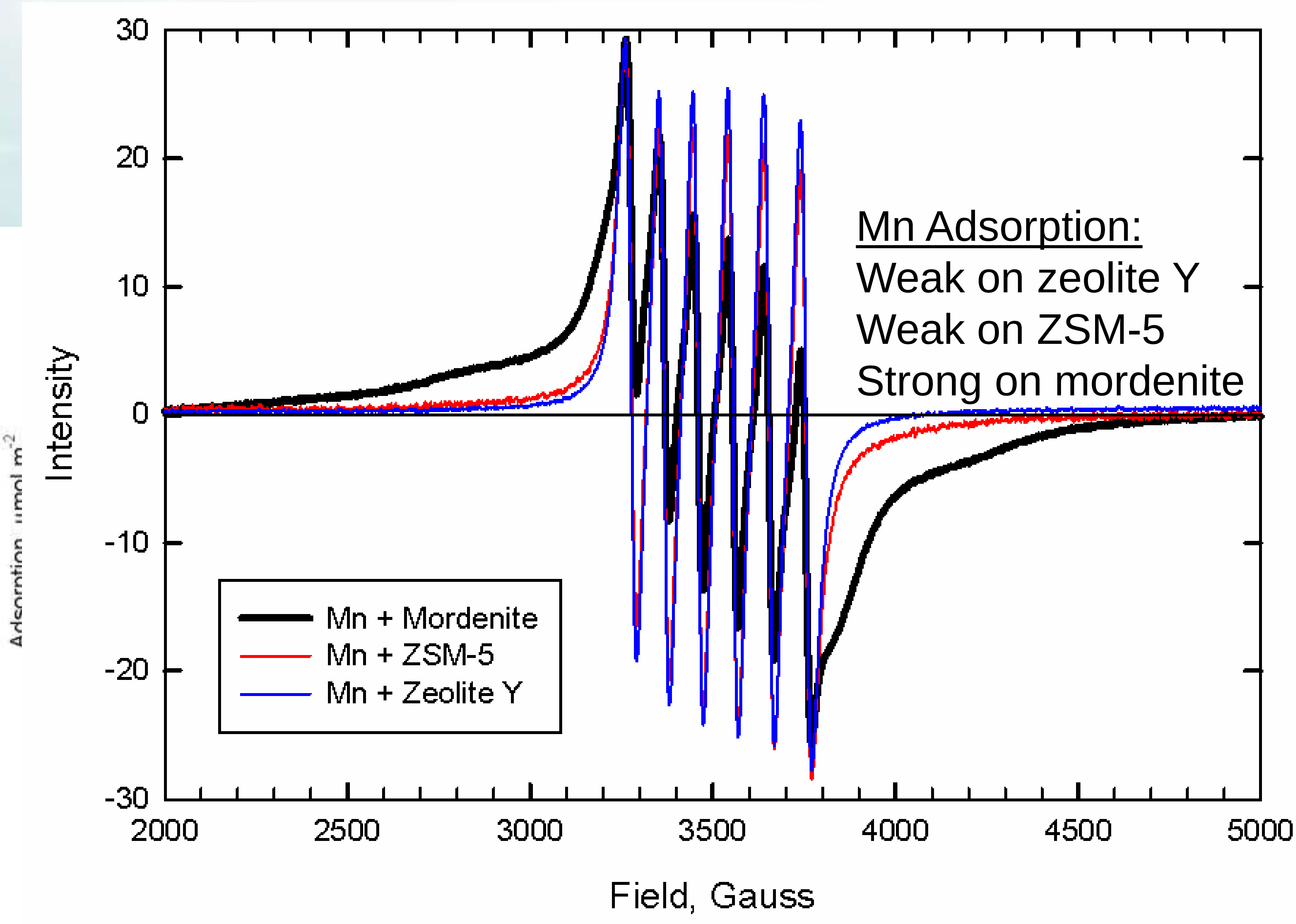
NMR and Divalent Ions

- NMR can’t analyze metallic elements
- NMR works based on an element’s precession frequency.
  - Difficult to analyze for any of the Group 2 elements due to low precession frequencies
- Need to address adsorption mechanisms of divalent ions on zeolites to completely prove the NISE theory

Group / Period	1	2
1	1 H 1.008	
2	3 Li 6.94	4 Be 9.0122
3	11 Na 22.990	12 Mg 24.305
4	19 K 39.098	20 Ca 40.078
5	37 Rb 85.468	38 Sr 87.62
6	55 Cs 132.91	56 Ba 137.33
7	87 Fr [223.02]	88 Ra [226.03]

EPR Spectroscopy

- EPR spectroscopy works like NMR, but on the electrons instead of the nucleus
- The study used a Bruker 380E 9.5 GHz X-band spectrometer with a WD14838 probe on Mn^{2+}

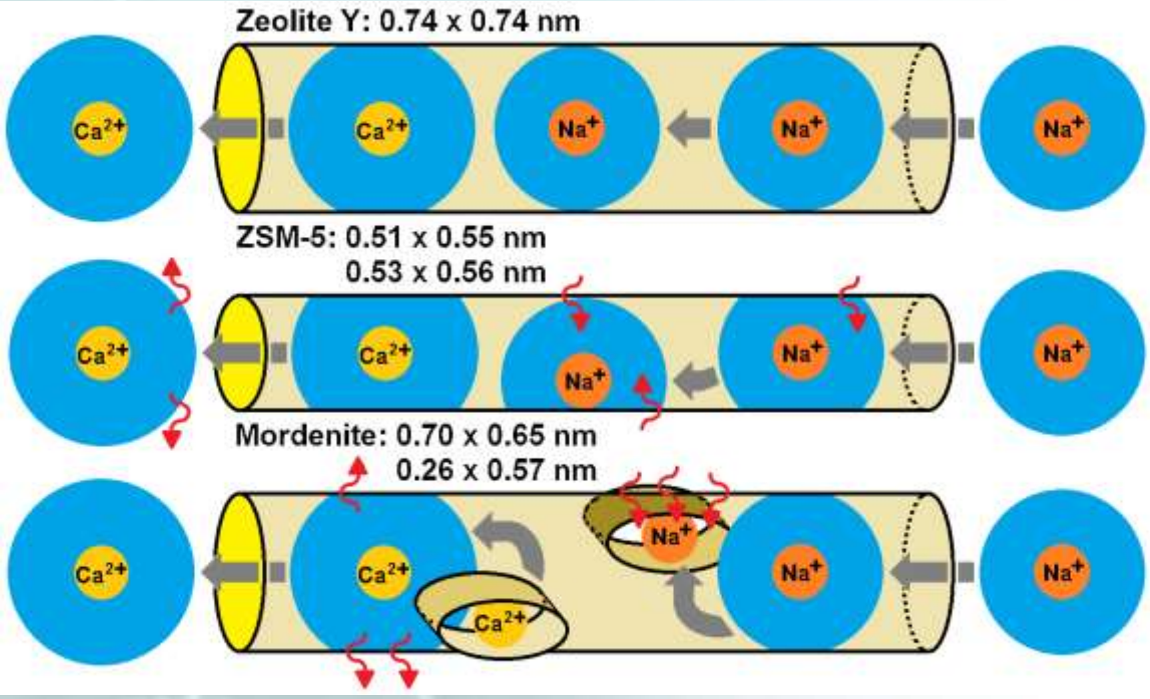

Mn Adsorption:
Weak on zeolite Y
Weak on ZSM-5
Strong on mordenite
Intensity
Field, Gauss
30
20
10
0
-10
-20
-30
2000
2500
3000
3500
4000
4500
5000
Mn + Mordenite
Mn + ZSM-5
Mn + Zeolite Y

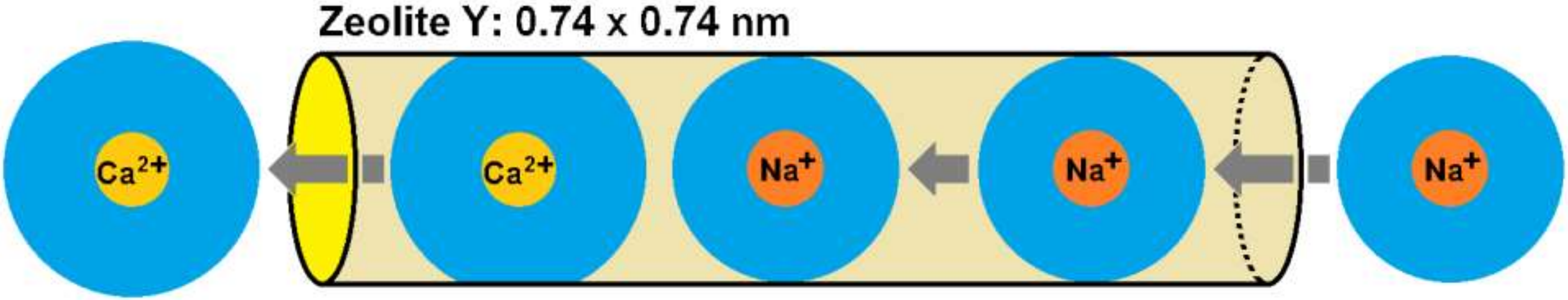
Summary of NMR/EPR

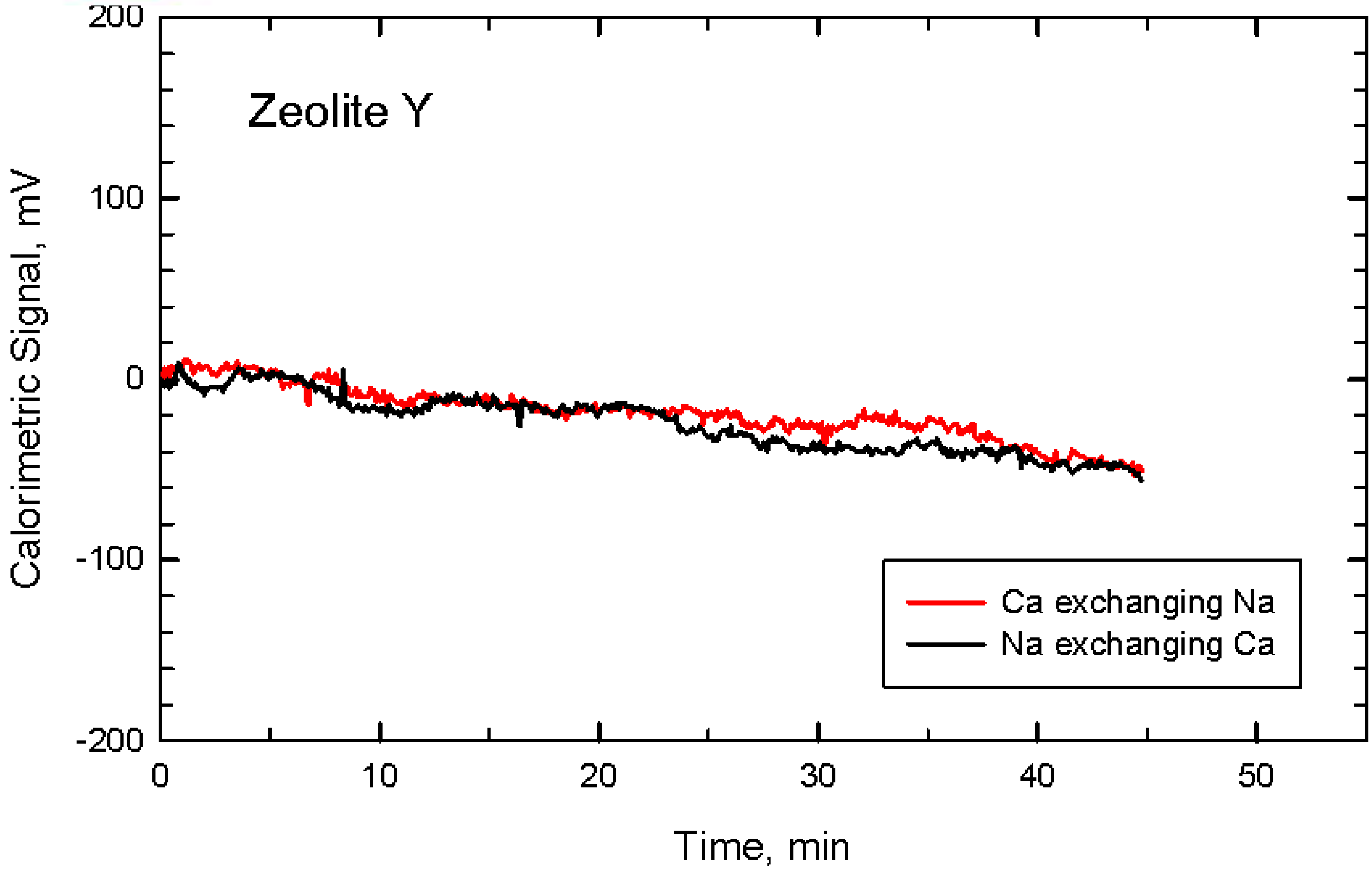
- NMR showed outer-sphere Na adsorption on zeolite Y & inner-sphere Na adsorption on ZSM-5 and mordenite
- EPR showed outer-sphere Mn adsorption on zeolite Y and ZSM-5 & inner-sphere Mn adsorption on mordenite
- These data match the predictions of the NISE model

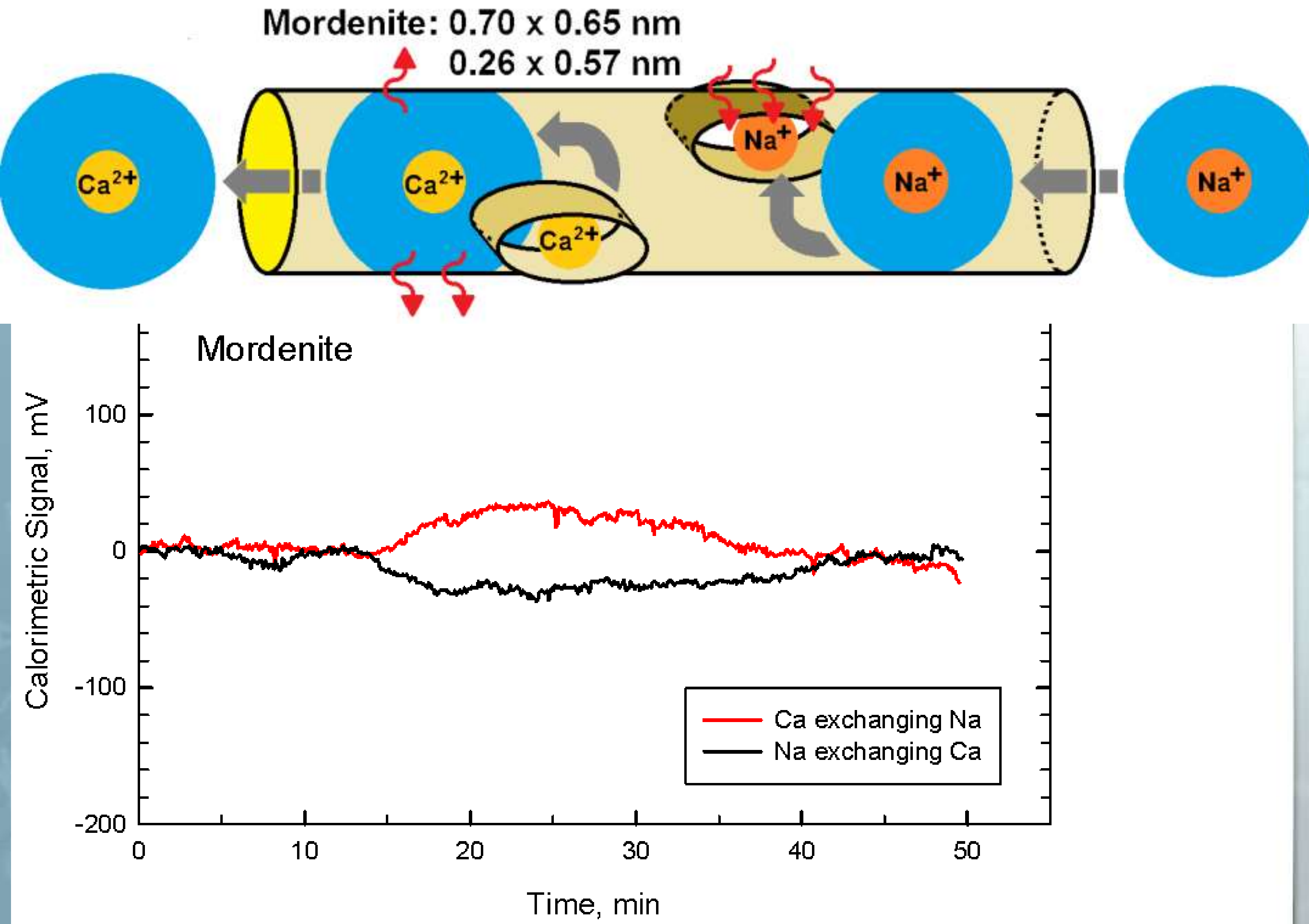
Calorimetry

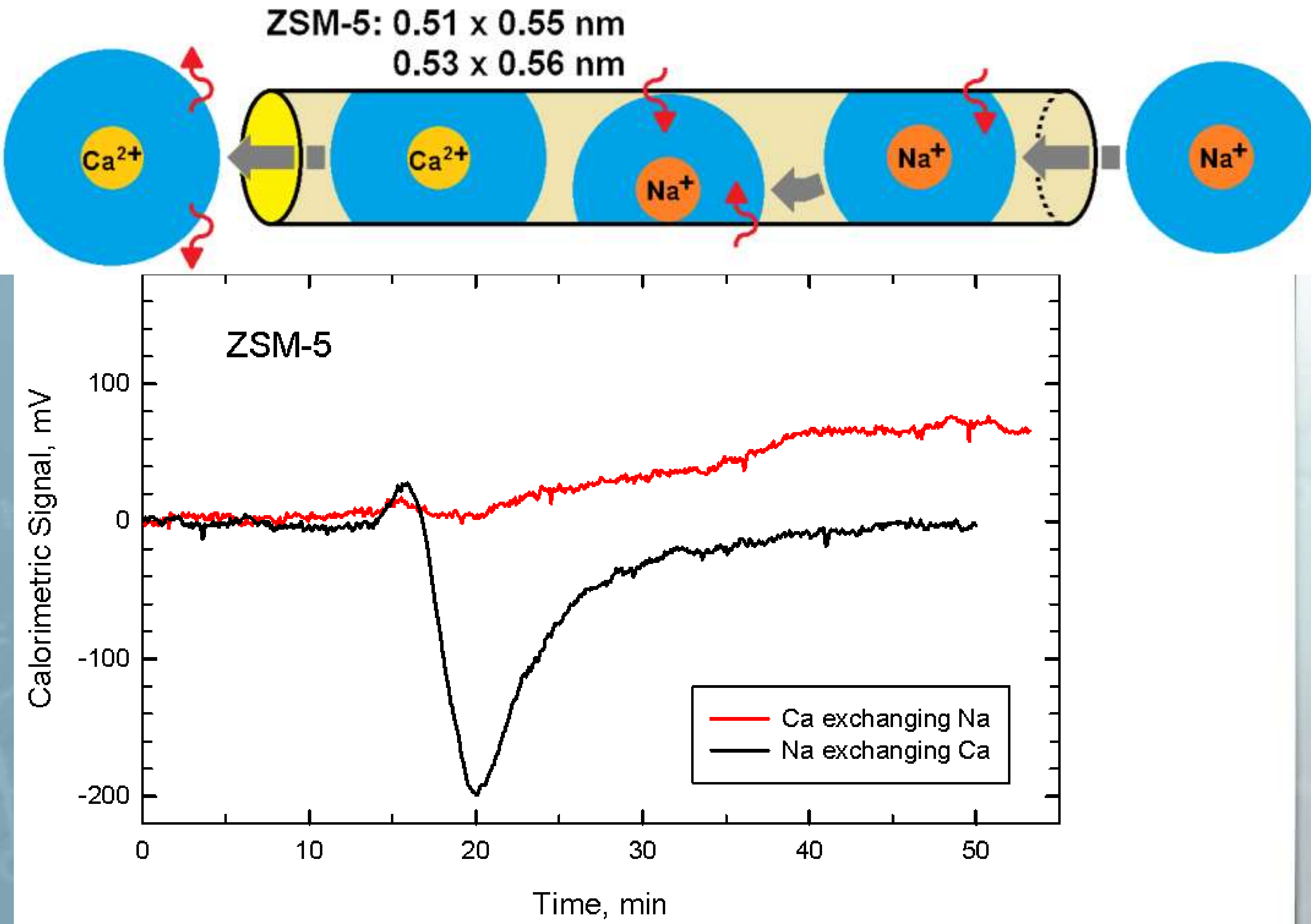
- Calorimetry measures the heat of reactions
- Flow calorimetry can compare the heat of exchange between Na and Ca on the zeolite minerals




Zeolite Y: 0.74 x 0.74 nm
Ca2+
Ca2+
Na+
Na+
Na+


Zeolite Y
Calorimetric Signal, mV
200
100
0
-100
-200
0
10
20
30
40
50
Time, min
Ca exchanging Na
Na exchanging Ca


Mordenite: 0.70 x 0.65 nm
0.26 x 0.57 nm
Ca2+
Ca2+
Ca2+
Na+
Na+
Na+
Mordenite
Calorimetric Signal, mV
100
0
-100
-200
0
10
20
30
40
50
Time, min
Ca exchanging Na
Na exchanging Ca


ZSM-5: 0.51 x 0.55 nm
0.53 x 0.56 nm
Ca2+
Ca2+
Na+
Na+
Na+
ZSM-5
Calorimetric Signal, mV
100
0
-100
-200
0
10
20
30
40
50
Time, min
Ca exchanging Na
Na exchanging Ca

Presentation Outline

I. The Nanopore Inner-Sphere Enhancement (NISE) Effect

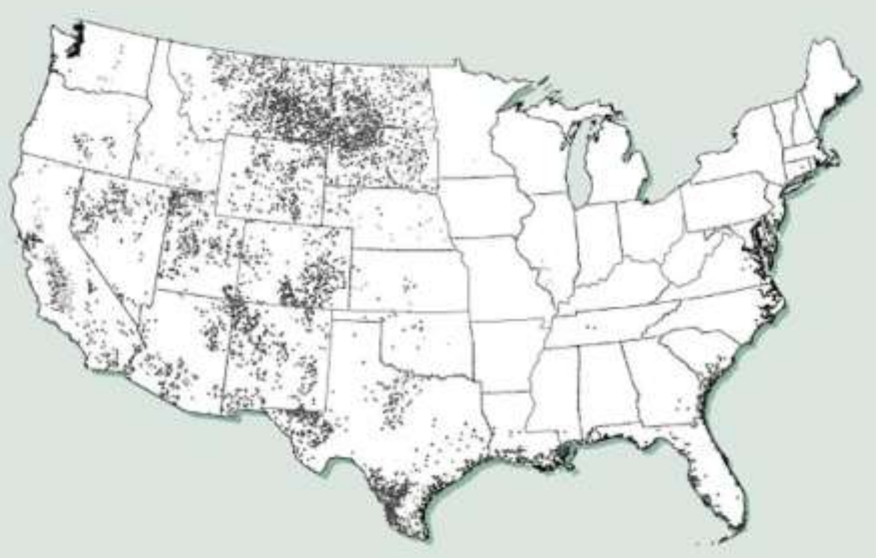
II. Investigation of the NISE Effect for cation adsorption on zeolites

III. Confirmation of the NISE Effect using NMR / EPR Spectroscopy and Calorimetry

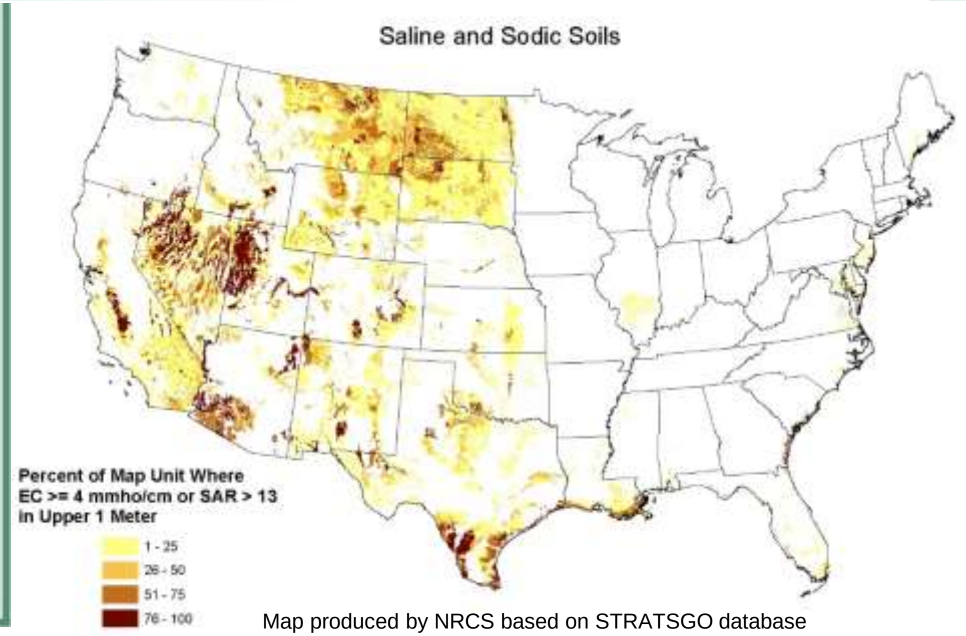
IV. **Application** of the NISE Effect in a Column Study

Sodic Soils

- Sodic soils affect a significant area of the US. Each dot below represents 10,000 acres of sodic soil.
  - ND estimates losses due to sodic soils of $50-$90 million per year
- Sodic soils strongly retain Na to the exclusion of many other ions
- Sodic soils are clay-rich & 2:1 interlayers can reach NISE sizes



From NRCS, c/o Brady & Weil, 2008



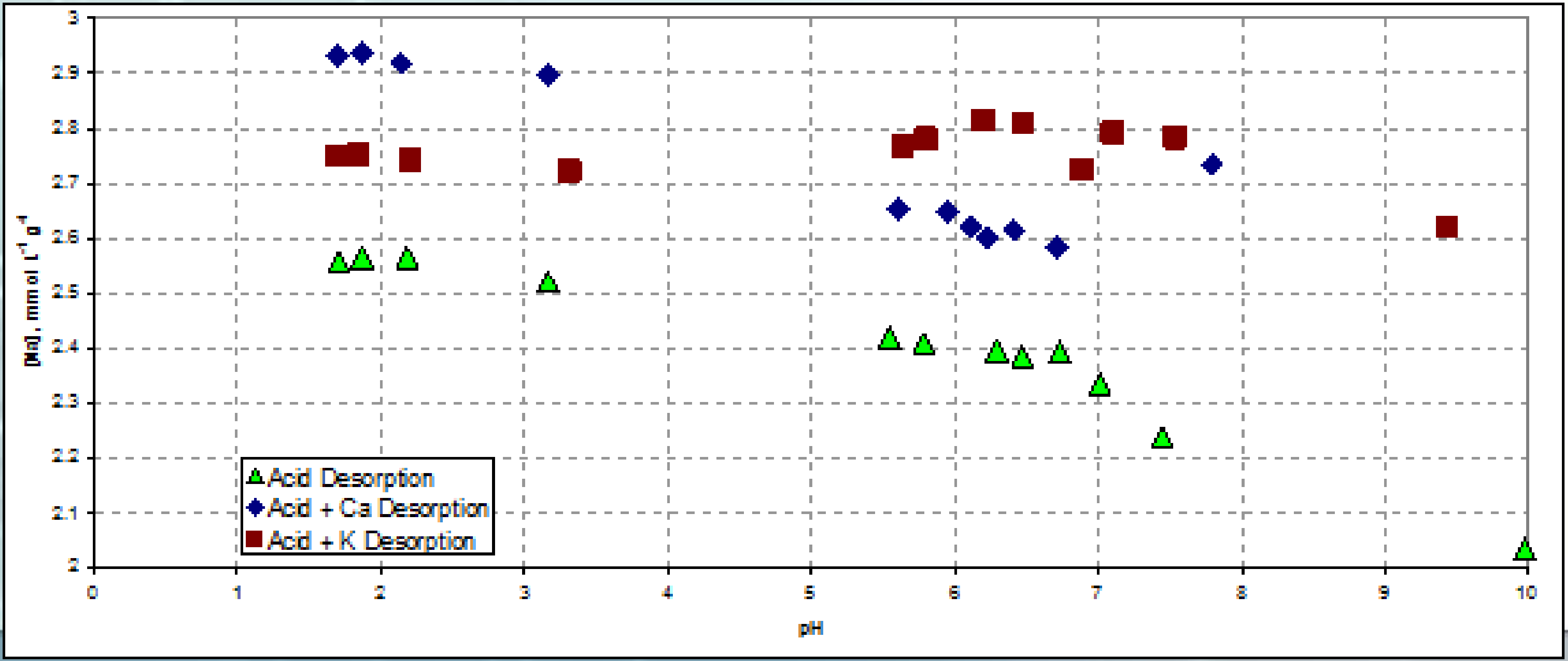
Map produced by NRCS based on STRATSGO database

Sodic Soils

- How strongly is Na retained in sodic soils?

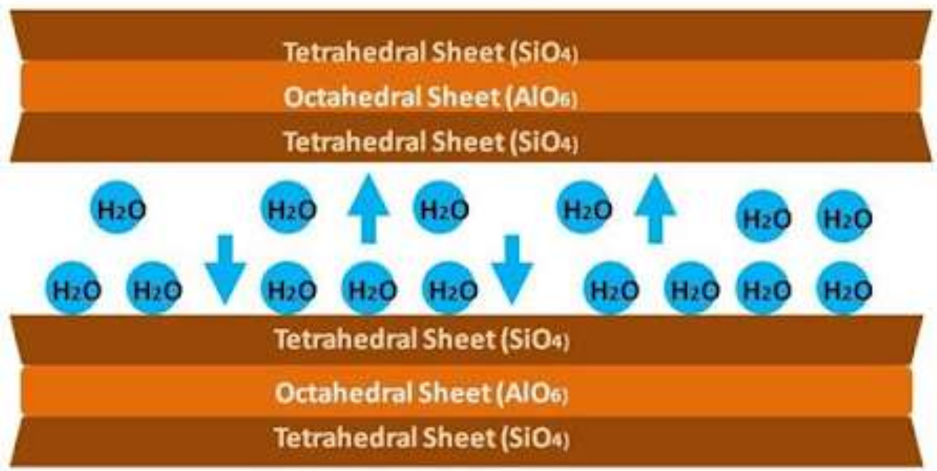
Sodic Soils

- Initial desorption experiments on sodic soils showed a Na desorption edge at pH 7 (very weakly held)
- This was likely due to high liquid to solid ratio in batch



Sodic Soils

- As water fills clay inter-layers, they expand
- Batch experiments have a high water to solids ratio
- If clays expand, any NISE effect will cease

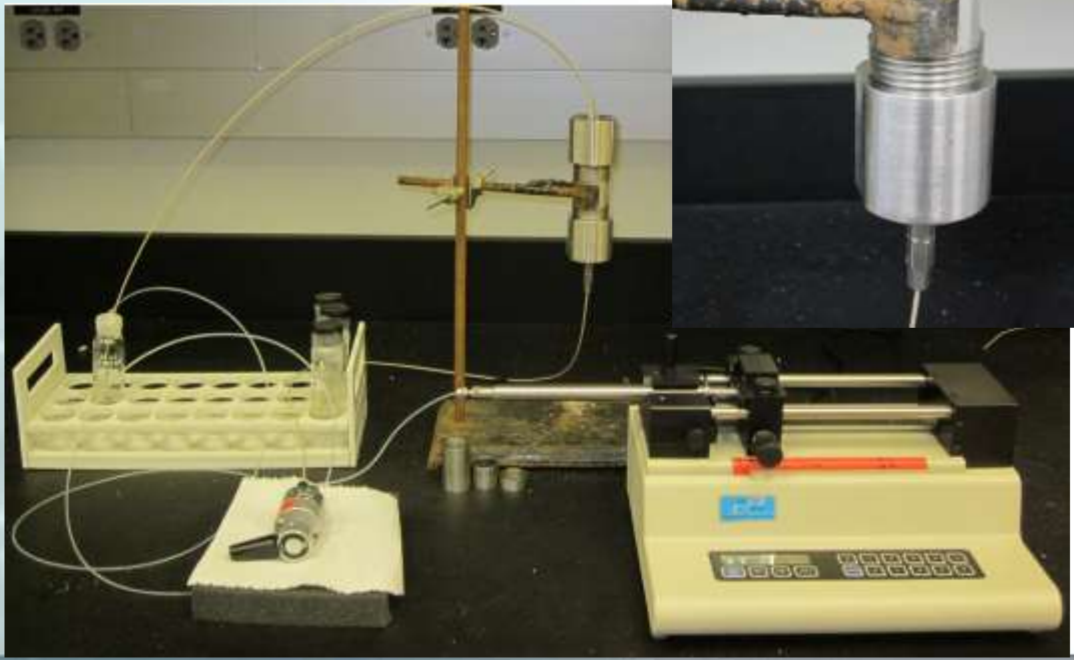


http://lh3.ggpht.com/_6LWjP0sZ22w/S4stYiWRxTI/AAAAAAAAHgA/QYhLzCxACso/Smectite%20Expansion%5B4%5D.jpg

- Sodic soils tend to be dense and tightly packed
- This would tend to prevent clay interlayer expansion
- A column study can attempt to recreate these conditions

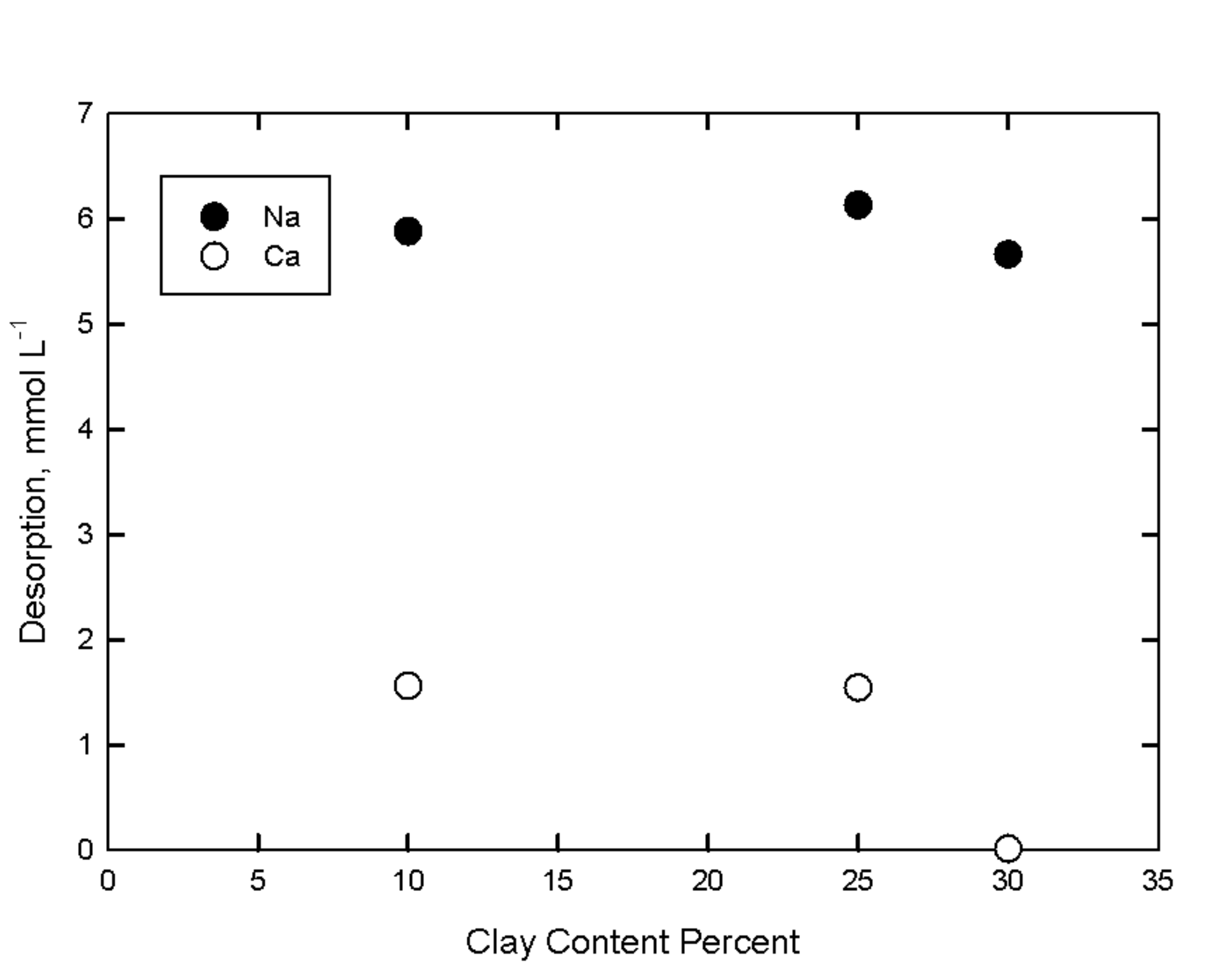
Column Study

- Stainless steel column filled with sand mixed with a Na-montmorillonite. Column is pressurized so clay cannot expand as easily.
- Na retention measured at various clay contents



Column Study

- [Na] desorbed remained mostly flat with ↑ [clay]
- [Ca] desorbed dropped sharply between 25% and 30% clay
- Pump failed above 30% clay, likely due to low hydraulic cond.



Conclusions

- The NISE effect offers a new model for explaining counterintuitive ion exchange reactions inside small confining environments such as zeolite nanopores
- The predictions of the NISE model have been directly verified through NMR, EPR, and calorimetry
- Attempts to replicate the NISE effect with 2:1 clay interlayers in a column study showed interesting preliminary results. More work is required in this area

References

Brady, N.C., and R.R. Weil. 2008. The Nature and Properties of Soils, 14th Edition. Prentice Hall.

Ferreira, D.R., and C.P. Schulthess. 2011. The Nanopore Inner-Sphere Enhancement (NISE) Effect: Sodium, potassium, and calcium. Soil Sci. Soc. Am. J. 75: 389-396.

Ferreira, D.R., C.P. Schulthess, M.V. Giotto. 2012a. An investigation of strong sodium retention mechanisms in nanopore environments using nuclear magnetic resonance spectroscopy. Environ. Sci. Technol., 46: 300-306.

Ferreira, D.R., C.P. Schulthess, J.E. Amonette, and E.D. Walter. 2012b. An Electron Paramagnetic Resonance Spectroscopy Investigation on the Retention Mechanisms of Divalent Cations in Zeolite Nanopores. Clay Clay Miner. 60 (6): 588-598.

Ferreira, D.R., C.P. Schulthess, and N.J. Kabengi. 2013. Calorimetric Evidence in Support of the Nanopore Inner-Sphere Enhancement (NISE) Theory on Cation Adsorption. Soil Sci. Soc. Am. J., 77:94-99

Schulthess, C.P., R.W. Taylor, and **D.R. Ferreira**. 2011. The Nanopore Inner-Sphere Enhancement (NISE) Effect: Sodium an nickel. Soil Sci. Soc. Am. J. 75: 378-388.

Schulthess, C.P. 2005. Soil chemistry with applied mathematics. Trafford Publ., Victoria, BC, Canada.

Hummer, G., L.R. Pratt, and A.E. García. 1996. On the free energy of ionic hydration. J. Phys. Chem. 100:1206−1215.

Questions?